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RAMAN STUDY OF NEUTRON
IRRADIATED GaAs

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and E.R. Weber

July 1984

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RAMAN STUDY OF NEUTRON IRRADIATED GaAs

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Raman scattering with near band gap excitation has been used to study fast neutron damaged GaAs. In addition to disorder activated first order scattering from zone edge acoustic phonons we observe a new peak that is attributed to a resonant mode associated with an intrinsic defect of GaAs, an As vacancy being the most likely candidate.

I. Introduction

The Raman scattering cross section possesses a fundamental dependence on the microscopic structure and symmetry of the scattering medium. Raman measurements thus have the ability to probe the nature of the disorder present in damaged material. For example, it is possible to observe vibrational modes associated with specific defects [1].

The dominant deep levels in semi-insulating liquid encapsulated Czochralski (LEC) grown GaAs are thought to be due to intrinsic defects. In this paper we report the results of a Raman study conducted in a high quality GaAs single crystal that has been damaged by fast neutron irradiation. We thus can probe disorder associated with the intrinsic defects which are expected to be present in high concentrations in such material. For incident photon energies at or below the E_0 gap we observe a Stokes Raman spectrum that closely resembles the acoustic phonon density of states in the range 20 to 260 cm^{-1} with the exception of a sharp (FWHM $< 10 \text{ cm}^{-1}$) peak located at 227 cm^{-1} . The "density-of-states-like" spectrum has been observed previously in a variety of systems [2-5] and is attributed to disorder activated first order Raman scattering (DAFORS). On the other hand, the sharp peak at 227 cm^{-1} has not been observed before and is not readily attributed to DAFORS. We present evidence that it is due to a resonant vibrational mode associated with an intrinsic defect in GaAs. Based on the observed symmetry and annealing behavior of the mode we conclude it is most likely a breathing mode of an As vacancy.

II. Experimental

The starting material for these experiments was semi-insulating (LEC) grown GaAs. Irradiation with a flux of $3 \times 10^{17}/\text{cm}^2$ fast (50keV) neutrons was performed at the FRJ-1 reactor of the Kernforschungsanlage Juelich under conditions similar to those described by Worner et. al. [6]

After irradiation the band edge luminescence is found to be completely quenched, thus making it possible to observe weak Raman scattering near the E_0 gap. For comparison we have also studied Cr-doped ($10^{17}/\text{cm}^3$) horizontal Bridgman grown GaAs. In this case the large Cr concentration effectively quenches the luminescence.

The GaAs samples were placed in an optical dewar and cooled to temperatures between 10 K and 100 K by flowing helium or nitrogen gas. Raman spectra were recorded in a backscattering geometry on (111) surfaces. The near band gap excitation (~ 200 mW in the range 11800 - 12600 cm^{-1}) was provided by a Styryl 9 dye laser pumped by an Ar^+ laser. Spectra were also recorded using the 19430 cm^{-1} line of the Ar^+ laser directly. Scattered light was dispersed by a $3/4$ m double monochromator and detected as single photons by a photomultiplier tube with a S-20 response that cuts off sharply below 11500 cm^{-1} . The spectra were corrected for distortion produced by the spectral response of the detection system by using the measured spectrum of a quartz halogen lamp for normalization.

III. Results

Figure 1 shows a series of Stokes Raman spectra in the range 20 to 260 cm^{-1} using a configuration in which the incident and scattered polarizations are parallel to one another. All were recorded with the sample at 100 K. Figures 1b and 1c contain the results for the Cr-doped and neutron irradiated samples obtained with 11823 cm^{-1} excitation. The rather large error bars are due to the fact that the signal was rather weak (~ 20 counts/sec). For comparison figure 1a shows the spectrum of unirradiated LEC-GaAs sample which is dominated by allowed 2 phonon overtone scattering [7]. The incident photons were at 19430 cm^{-1} in this case since strong luminescence precluded the use of near band gap excitation.

We note that the spectrum for the neutron irradiated sample (fig.1c) qualitatively resembles those found in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ [3-5] and in ion implantation damaged GaAs [2]; where the observed structures have been associated with the one acoustic phonon density of states. (E. g., peaks B and C in fig. 1c coincide with the LA and TA critical points.) An exception is the sharp ($\text{FWHM} < 10$ cm^{-1}) peak observed at 227 cm^{-1} (labelled A in fig. 1c). Polarization studies demonstrate that peaks A, B and C all exhibit Γ_1 symmetry.[8] The lineshape of the LO phonon observed in the neutron irradiated sample (not shown) is essentially indistinguishable from that found in undamaged material whereas both in $\text{Ga}_x\text{Al}_{1-x}\text{As}$ [4] and ion implantation damaged [2] GaAs the LO phonon was found to exhibit an asymmetric and red-shifted lineshape. The spectrum for the Cr doped sample (fig. 1b) can be interpreted as due to a superposition of the spectra observed in the unirradiated and the neutron irradiated samples with the exception that peak A is absent.

We have also investigated the excitation energy dependence of the Raman spectra for the neutron irradiated samples. Using 19430 cm^{-1} excitation the spectrum was found to closely resemble the two-phonon density of states-like behavior observed in the undamaged sample (fig.1a), a result very different from the infrared results of figure 1c. The dependence of the spectra on the photon energy in the vicinity of the E_0 gap will be presented elsewhere. Figure 1d shows one spectrum re-

corded with an incident photon wave number of 12307 cm^{-1} . It is clear that the dependence of the intensity of peak A on the energy of the exciting photon is qualitatively different from that of peaks B or C. When the sample temperature is lowered to 10 K and using infra-red excitation the spectra are essentially unchanged with the exception that the intensity of peak A increases by a factor of 3 relative to peaks B and C.

To help identify the defects responsible for our observed spectra we subjected several pieces of our sample to isochronal (one hour) annealing treatments at temperatures ranging from 220 C to 600 C. The results are shown in figure 1e. Peaks A, B and C remain unchanged when the sample is annealed to 220 C but disappear after annealing at 320 C. By 440 C a weaker "density-of-states-like" structure reappears. For the sample annealed to 600 C (not shown) a strong band edge luminescence was observed to have returned and masks whatever Raman signal might be present.

IV. Discussion

Several previous studies [9,10] have focused on the nature of the damage produced by neutron irradiation of GaAs and the following picture has emerged. The volume surrounding a "primary knock on" consists of damaged material that remains basically crystalline. For samples irradiated with a flux of 3×10^{17} neutrons/cm² these damaged cores occupy roughly 5% of the total sample volume. It has been proposed that the primary defects are interstitial-vacancy pairs that are accompanied by local strains. Defect complexes are not thought to be produced in large numbers.

With the above in mind we interpret our results. Based on the strong similarity between figure 1c and the Raman spectra that have been observed in other disordered systems [2-5] we conclude that the structure in figure 1c is largely due to DAFORS. As in other observations of DAFORS [2-5] the scattering is predominately of Γ_1 symmetry. The fact that the LO phonon lineshape we observe is unchanged from that found in an undamaged crystal can be understood within the framework of the above picture of an inhomogeneously damaged sample. The spectra we observe are a superposition of allowed first order scattering (sharp LO and TO peaks) from the relatively undamaged regions that occupy 95% of the sample volume and weak DAFORS from the damaged cores. As mentioned above, peak A in figure 1c constitutes a significant deviation from the "density-of-states-like" DAFORS spectrum found in other systems. In trying to identify the nature of this peak we make the following observations. We rule out the possibility that it is due to a two phonon overtone process because the corresponding one phonon structure is not observed. We also rule out the possibility that is due to a two phonon combination process involving emission of optical phonon and absorption of acoustic phonon because peak A is still strong at 10 K and because the corresponding two phonon emission process is not observed. The absence of peak A in the Cr doped sample and in the ion implantation damaged GaAs reported by Tiong et. al. [2] implies that it is associated with the presence of a specific defect introduced in relatively large concentrations by neutron irradiation.

Two plausible choices remain. The first is that peak A is due to a bulk phonon mode (it coincides with the LA(X) critical point) that is for some reason preferentially enhanced because of matrix element effects.

The second is that peak A is due to a resonant vibrational mode, i.e. a quasi-localized vibration associated with a particular intrinsic defect. While we cannot definitely eliminate the former possibility we believe that the latter is much more likely. This conclusion is based on the observations that the dependence of peak A on the energy of the exciting photon (fig 1 c and d) and on the sample temperature are clearly different from those of bulk phonon peaks B and C.

Which of the intrinsic defects that are possible in GaAs are likely to be responsible for peak A? The observed Γ_1 symmetry of the Raman scattering make it unlikely that a complex is involved. The list of candidates then consists of simple intrinsic point defects: $I_{Ga,As}$, $V_{Ga,As}$, As_{Ga} and Ga_{As} . The annealing behavior allows some of these to be ruled out. For example, ESR measurements in our sample show that it contains $10^{18}/cm^3$ As_{Ga} antisite defects.[15] Measurements by Worner et al. [6] have shown that after one hour isochronal annealing the concentration of As_{Ga} as determined by ESR remains constant to 400 C above which there is a sharp drop (~ 100 -fold). From our annealing results we conclude that the As_{Ga} defects are not responsible either for peak A or for the bulk of the DAFORS we observe. However it is possible that the weak structure apparent in the sample annealed to 440 C is due to As_{Ga} .

GaAs that has been damaged by a variety of methods exhibits well defined annealing stages at 225 C [11]. In particular, Laithwaite and Newman [10] and Coates and Williams [9] both observe such an annealing stage in neutron damaged material. Pons and Bourgoin [12] also observe this stage in electron irradiated GaAs and present strong evidence that it is due to the annealing of a simple defect formed by displacement of the As sublattice (i.e. V_{As} , As_{Ga} or I_{As}). Pons et al. [13] and Cheng et al. [14] show that the vacancy is the more likely possibility. On this basis we conclude that peak A is most likely associated with V_{As} , the observed Γ_1 symmetry suggesting a breathing mode. This proposed identification should be checked by a theoretical calculation of the vibrational properties of vacancies and interstitials in GaAs. If this identification of the 227 cm^{-1} Raman mode is confirmed by theoretical calculation, it will be a powerful means to study the properties of As vacancies in GaAs.

Finally, we remark that the results obtained with 19430 cm^{-1} excitation illustrate the importance of a judicious choice of photon energy when using Raman scattering as a probe of disorder. In this work the use of infra-red excitation allowed disorder related processes to be preferentially enhanced relative to the two phonon overtone scattering that dominates the spectra obtained with 19430 cm^{-1} excitation.

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Figure Captions

Figure 1 - Raman Spectra of GaAs. Excitation wave numbers are indicated in the figure. a) Undamaged LEC sample. b) $10^{17}/\text{cm}^3$ Cr doped sample. c) Fast neutron irradiated sample. d) Same sample as in (c) but with excitation at 12307 cm^{-1} . e) Same sample as in (c) after 1 hour anneal at temperatures indicated.

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